

AD/A-002 234

CORROSION OF ALUMINUM ALLOYS IN EXFOLIATION-RESISTANT TEMPERS EXPOSED TO MARINE ENVIRONMENTS FOR 2 YEARS

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Annapolis, Maryland

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condition exposed to the same environments showed some pitting and edge attack but did not indicate a long-term corrosion problem.

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ADMINISTRATIVE INFORMATION

This report was prepared under TOP 21, Task Area SF 54 541 702, Task 14626 on Engineering Properties of Aluminum Alloys for Lightweight Ship Structures, Work Unit 2814-143. The investigation was sponsored by the Naval Sea Systems Command (SEA 035). Mr. B. B. Rosenbaum (SEA 03523) is the program manager, and Mr. T. C. West, Naval Ship Engineering Center (SEC 61010), is the technical agent.

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INTRODUCTION

The aluminum-magnesium alloys, 5086, 5083, and 5456, are attractive materials for naval construction because of their marine corrosion resistance, high strength-to-weight ratio, and weldability. The alloys have been used by the Navy for light-weight superstructures and as the primary structural metal for high-speed, high-performance ships and craft. The most desirable combination of properties in sheet and plate was achieved in a mildly cold-worked temper (quarter-hard) designated as 5086-H32, 5083-H321, and 5456-H321. However, under certain conditions, exfoliation corrosion problems were experienced with the standard temper. Exfoliation or lamellar corrosion is a type of intergranular corrosion causing delamination in thin plate material.

To solve the exfoliation problem, the aluminum industry developed rolling procedures for tempers meeting the mechanical property requirements specified for the H32 and H321 tempers and having a metallurgical structure resistant to exfoliation-type corrosion.^{1,2} These tempers for sheet and plate high-Mg, 5000-series alloys are designated H116, developed by Reynolds Metals Company, and H117, developed by Alcoa. These exfoliation-resistant tempers are included in Interim Federal Specifications QQ-A-00250/19 and QQ-A-00250/20 for 5086 and 5456 alloys, respectively.

The purpose of this investigation was to study the corrosion behavior of the three high-strength, Al-Mg alloys, 5086, 5083, and 5456, in the exfoliation-resistant tempers when exposed to three marine environments. This report summarizes the results for exposure durations of 6 months, 1 year, and 2 years.

METHOD OF INVESTIGATION

Panels were cut from plates of 5086-H116, 5086-H117, 5083-H116, 5456-H116, and 5456-H117 alloys. The test panel size, thickness, and source are listed in table 1. Specimen panels were exposed with the as-rolled surface finish and with saw-cut or sheared edges.

Panels were tested in two conditions, viz., as-rolled and sensitized. The sensitizing treatment, 1 week at 100° C* in a laboratory oven, is an accelerated aging process to simulate the worst possible condition of the alloy microstructure after long-term service. Such a condition might occur in deck and superstructure applications where exposure to the sun and tropical temperatures are experienced.

¹ Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

*Abbreviations used in this text are from the GPO Style Manual, 1973, unless otherwise noted.

TABLE 1
MATERIALS UNDER INVESTIGATION

Alloy and Temper	Plate Thickness inch	NSRDC* Code Letters	Test Panel Size inch	Source
5086-H116	1/4	EST	12 x 3	Reynolds Metals Company
5086-H116	3/4	ESX	12 x 3	Reynolds Metals Company
5086-H117	1/4	ETJ	8 x 3	Alcoa
5083-H116	1/4	ETC	12 x 3	Reynolds Metals Company
5083-H116	1/2	ETD	12 x 3	Reynolds Metals Company
5456-H116	1/4	ESY	12 x 3	Reynolds Metals Company
5456-H116	1/2	ESZ	12 x 3	Reynolds Metals Company
5456-H117	1/4	ETK	8 x 3	Alcoa
5456-H117	1/2	ETF	12 x 3	Alcoa

*NSRDC - Naval Ship Research and Development Center

Panels in both conditions were exposed to three different marine environments at the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina. The three environments were:

- Completely submerged in a trough of slowly flowing sea water (2 to 3 ft/s).
- Exposure in a "splash and spray" zone which is the level of wave breaking.
- Exposure to a marine atmosphere 80 feet from the shore.

Where sufficient material was available, duplicate specimens were tested for every exposure condition. A total of 282 specimens was included in the program. Specimens were removed after exposures of 6 months, 1 year, and 2 years. Note that specimens were not cleaned, inspected, and reexposed; rather, each exposure was for the total duration, and specimens were left undisturbed during the entire period of the specific test.

RESULTS AND DISCUSSION

MICROSTRUCTURES

Exfoliation or lamellar corrosion is a specific type of intergranular corrosion attack which can occur along grain boundaries parallel to the metal surface of aluminum products having an elongated grain structure, such as light gage plate or extruded shapes. The generation of corrosion products forces the

uncorroded layers apart and causes the metal to swell and delaminate or flake apart. For those Al-Mg alloys containing greater than 3% Mg, susceptibility to exfoliation is dependent on the amount of cold work introduced.³ Plate and sheet having been severely rolled show a striated grain structure with precipitate in the grain boundaries as a continuous line (figure 1). The precipitate (Mg_2Al_3) is anodic to the solid solution in the grain bodies and corrodes preferentially.³ It is the continuity of the precipitate which makes the structure liable to exfoliation attack.

The H32 and H321 tempers apply to products which are strain hardened and then stabilized by a low-temperature heat treatment to slightly lower the strength and to increase ductility and stress-corrosion resistance. This process can result in a microstructure in which the precipitate is present in a continuous line. Microstructures of as-received 5456-H321 plate and the same material sensitized (1 week at 100° C) are shown in figure 1. With heavy lamellar precipitate already present in the as-received microstructure, sensitizing had little effect in furthering the precipitation.

The new tempers, H116 and H117, apply to products which are strain hardened less than quarter-hard and do not undergo a stabilizing heat treatment. The objective of these tempers is to provide material having a metallurgical structure with a discontinuous network of precipitate. Such a structure should not be susceptible to exfoliation. Figures 2 through 10 show the microstructures of the new tempers for the alloys and plate thicknesses under the present investigation in both as-received and sensitized conditions. Note the discontinuous network of the precipitate in the as-received plates.

Interim Federal Specifications QQ-A-00250/19 (Navy-Ships) for 5086 plate and sheet and QQ-A-00250/20 (Navy-Ships) for 5456 plate and sheet in the H116 and H117 tempers require, as part of the material qualification procedure, that samples of production lots be examined metallographically. The examination must show a microstructure predominantly free of a continuous grain boundary network of Al-Mg precipitate. The as-received microstructures of plates of all alloys and thicknesses for the H116 and H117 tempers in this study meet the requirement (figures 2 through 10).

The H116 and H117 tempers represent two different approaches for providing a discontinuous precipitate network. In the H116 temper, the precipitate is dispersed throughout the metal in disconnected paths, while the H117 process prevents the formation of paths of precipitate along the grain boundaries. It was observed that in the as-received condition, the alloys in H117 temper (figures 4, 9, and 10) had a sparse population of precipitates in comparison to those in H116 temper. However, after the sensitizing treatment, the H117 tempers show heavy, continuous "stringers" of precipitate, whereas the alloys in the H116 temper show only a slight increase in precipitate density and continuity. It seems,

therefore, that inherent in the H116 tempering procedure is a stabilizing process which inhibits further growth of precipitate. The H117 tempers appear to hold much Mg in solution. Consequently, this less stable condition is more responsive to the sensitizing treatment.

The sensitization treatment may be more severe than natural aging. Sensitization treatments may be considered a means of obtaining a conservative evaluation of long-term corrosion performance when long-term data are not available, and the long delay involved in complete evaluation under conditions of natural aging and exposure is unreasonable.

CORROSION

The results of exposure to the three environments are summarized in table 2 for panels exposed to marine atmosphere, in table 3 for panels exposed to splash and spray, and in table 4 for the fully submerged panels. The results are given in terms of corrosion rates in mils per year, based on weight loss and exposed surface area. In general, the calculated rates for any exposure and condition were less than 1 mil/yr and decreased with time, i.e., the initial attack is highest.

The panels exposed to marine atmosphere and to splash and spray showed a scattered light pitting on surfaces, with a slightly greater intensity in the latter exposure. The pitting can best be described as "pinpoint" and of insignificant depth. The one exception to this general behavior was that of the sensitized, 1/4-inch-thick 5456-H117 panels. In both environments, the attack on these panels appeared as a minor scattered surface blistering. The attack was first noted after 1 year of exposure, being the only instance of increased corrosion rate at that time; however, the rates after 2 years of exposure show the attack to have virtually ceased.

Surface attack on the as-received and the sensitized 5456-H117 1/4-inch panels after 2 years of exposure to splash and spray and marine atmosphere is compared in figure 11. White corrosion product was present under the blisters, and an area about 1/2 x 1/8 inch near the edge of the sensitized panel exposed to splash and spray showed evidence of delamination (figure 12). Corrosion rates based on weight losses of the 1/4-inch panels ranged from nil to 0.10 mil/yr in both the splash and spray exposure and marine atmosphere.

TABLE 2
CORROSION TEST RESULTS FOR ALUMINUM ALLOYS IN
MARINE ATMOSPHERE 80 FEET FROM OCEAN

Alloy and Temper	Plate Thickness inch	Corrosion Rate mil/yr			Corrosion Description After 2 Years
		6 Months	1 Year	2 Years	
<u>As-Rolled Condition</u>					
5086-H116	1/4	0.10	0.09	Nil	
5086-H117	1/4	0.10	0.13	Nil	
5083-H116	1/4	Nil	0.11	Nil	
5456-H116	1/4	0.10	0.11	Nil	
5456-H117	1/4	0.10	0.13	0.10	Scattered light pitting
5083-H116	1/2	0.30	0.13	0.10	
5456-H116	1/2	0.35	0.13	0.05	
5086-H116	3/4	0.50	0.12	0.10	
<u>Sensitized Condition</u>					
5086-H116	1/4	Nil	0.17	Nil	Scattered light pitting
5086-H117	1/4	0.20	0.17	Nil	Scattered light pitting
5083-H116	1/4	Nil	0.33	Nil	Scattered light pitting
5456-H117	1/4	0.30	0.65	Nil	Moderate light blistering
5083-H116	1/2	0.40	0.31	0.05	Scattered light pitting
5456-H116	1/2	0.40	0.23	0.10	Scattered light pitting
5086-H116	3/4	0.50	0.26	0.10	Scattered light pitting

TABLE 3
CORROSION TEST RESULTS FOR ALUMINUM ALLOYS IN
SPLASH AND SPRAY ZONE

Alloy and Temper	Plate Thickness inch	Corrosion Rate mil/yr			Corrosion Description After 2 Years
		6 Months	1 Year	2 Years	
<u>As-Rolled Condition</u>					
5086-H116	1/4	0.10	0.11	Nil	
5086-H117	1/4	0.10	0.09	Nil	
5083-H116	1/4	Nil	0.07	Nil	
5456-H116	1/4	0.10	0.09	0.10	
5456-H117	1/4	0.1	0.13	0.10	Scattered light pitting
5083-H116	1/2	0.35	0.08	0.05	
5456-H116	1/2	0.35	0.13	0.10	
5086-H116	3/4	0.30	0.12	0.10	
<u>Sensitized Condition</u>					
5086-H116	1/4	0.15	0.14	Nil	Scattered light pitting
5086-H117	1/4	0.10	0.13	Nil	Scattered light pitting
5083-H116	1/4	0.25	0.17	Nil	Scattered light pitting
5456-H117	1/4	0.10	0.2	Nil	Moderate light blistering
5083-H116	1/2	0.30	0.13	0.10	Scattered light pitting
5456-H116	1/2	0.25	0.21	0.05	Scattered light pitting
5086-H116	3/4	0.40	0.14	0.10	Scattered light pitting

TABLE 4
CORROSION TEST RESULTS FOR ALUMINUM ALLOYS
FULLY SUBMERGED IN FLOWING SEA WATER

Alloy and Temper	Plate Thickness inch	Corrosion Rate mil/yr			Corrosion Description After 2 Years	Edge Attack After 2 Years
		6 Months	1 Year	2 Years		
<u>As-Rolled Condition</u>						
5086-H116	1/4	0.80	0.53	0.45	Light uniform attack, moderate slight pitting	Moderate
5086-H117	1/4	0.90	0.52	0.40	Light uniform attack, no pitting	None
5083-H116	1/4	0.75	0.47	0.40	Light uniform attack, minor incipient pitting	Very slight and local
5456-H116	1/4	0.80	0.48	0.40	Light uniform attack, no pitting	None
5456-H117	1/4	0.70	0.48	0.30	Light uniform attack, no pitting	None
5083-H116	1/2	0.85	0.47	0.50	Light uniform attack, minor incipient pitting	Moderate and local
5456-H116	1/2	0.70	0.50	0.45	Light uniform attack, minor incipient pitting	Moderate and local
5456-H117	1/2	0.60	0.50	-	Light uniform attack, no pitting*	None*
5086-H116	3/4	1.00	0.43	0.30	Light uniform attack, no pitting	Slight and local
<u>Sensitized Condition</u>						
5086-H116	1/4	0.70	0.57	0.40	Light uniform attack, no pitting	Slight
5086-H117	1/4	0.80	0.52	0.40	Light uniform attack, no pitting	None
5083-H116	1/4	0.70	0.51	0.80	Light uniform attack, severe shallow pitting	Severe
5456-H117	1/4	0.70	0.56	0.50	Light uniform attack, no pitting	None
5083-H116	1/2	1.15	0.56	0.40	Light uniform attack, minor shallow pitting	Moderate
5456-H116	1/2	1.85	1.02	1.15	Light uniform attack, minor incipient pitting	Severe
5456-H117	1/2	0.80	0.85	-	Light uniform attack, no pitting*	Severe*
5086-H116	3/4	1.10	0.55	0.40	Light uniform attack, no pitting	Moderate

*After 1 year in test.

The highest corrosion rates resulted from the fully submerged exposure where the surface generally showed a light, uniform corrosion with minor pitting in some cases. Severe edge attack occurred in most alloys and thicknesses in both the as-received and sensitized conditions. Based on weight loss, the average corrosion rate for the 1/4-inch-thick panels which experienced no edge attack (5086-H117, 5456-H116, and 5456-H117) was 0.80 mil/yr in the first 6 months (i.e., 0.40 mil of metal loss in 6 months). The average corrosion rate after the first year was 0.52 mil/yr (0.52 mil of metal loss) and 0.39 mil/yr after the second year (0.78 mil of total metal loss). Thus, the actual corrosion rate in the second 6 months was 0.24 mil/yr (or 0.12 mil of metal loss in the second 6 months) and 0.26 mil/yr in the second year (or 0.26 mil of metal loss in the second year). This analysis indicates that the general corrosion rate reduces to a low, uniform rate after the initial attack of the first 6 months.

The pitting attack on the fully immersed panel surfaces was minor and shallow in the alloys of H116 temper; alloys of the H117 temper experienced no significant local surface attack. Severe shallow pitting was experienced, however, in the sensitized 5083-H116, 1/4-inch plate, as shown in figure 13.

Edge attack generally occurred in the same panels that exhibited some form of pitting attack. Attack was most severe in the sensitized 5083-H116, 1/4-inch plate and sensitized 5456-H116, 1/2-inch plate. Figures 14 and 15 show the attack in these specimens compared to the as-received condition and different thicknesses. Although the attack occurred in some of the as-received plates, sensitized specimens showed the more severe attack. The alloys in the H117 temper did not exhibit edge corrosion except for the sensitized 1/2-inch-thick 5456-H117. Both the massive pitting and the severe edge attack were found to be conventional intergranular corrosion. By this process, corrosion of the grain boundaries tends to spread out in all directions, removing whole grains, and causing an area of intense local attack.

The slight pitting and edge attack in the as-received plates were insignificant and would probably be prevented in service by paint; however, buttering of exposed edges with weld metal below the waterline is suggested for complete immunity to edge attack. Although alloys in a sensitized condition showed an increased severity of pitting and edge attack, none of the observations indicates a corrosion problem beyond routine maintenance in the long-term usage of these alloys in marine applications.

In a previous investigation,⁴ the same alloys in several sheet gages in standard tempers (0, -H14, -H34, and -H321) were partially immersed in sea water for exposure times up to 7 years. General corrosion damage was mild, characterized by shallow pitting. The present study confirms the excellent marine corrosion resistance of the commercial 5000-series alloys in the new H116 and H117 tempers.

CONCLUSIONS

The results of the investigation reported herein may be summarized as follows:

- Metallographic analysis of as-received plates of Al-Mg alloys 5086, 5083, and 5456 in H116 and H117 tempers in thicknesses from 1/4 to 3/4 inch showed structures with discontinuous or randomly dispersed precipitate network necessary for exfoliation resistance.
- The alloys in H117 temper showed continuous precipitate network after a sensitizing treatment. The same alloys in H116 temper realized only a slight increase in precipitate density and continuity, suggesting that the H116 temper produces material less susceptible to natural aging.
- The results of 2 years of exposure to marine environments (marine atmosphere, splash and spray, and fully submerged in sea water) indicate that alloys 5086, 5083, and 5456 in the H116 and H117 tempers have good corrosion resistance. No exfoliation attack was evident on any test panel.

TECHNICAL REFERENCES

- 1 - Brooks, C. L., "Aluminum-Magnesium Alloys 5086 and 5456-H116," Naval Engineers Journal, Vol. 82, No. 4, pp. 29-32 (Aug 1970)
- 2 - Wood, C., Jr., "Selecting Wrought Aluminum Alloys for Marine Use," Aluminum Company of America (June 1969)
- 3 - Binger, W. W., et al, "Resistance to Corrosion and Stress Corrosion," Aluminum, Vol. 1, Chapter 7, Amer. Soc. for Metals (1967)
- 4 - Niederberger, P. B., et al, "Corrosion and Stress Corrosion of 5000-Series Al Alloys in Marine Environments," Corrosion, Vol. 22, No. 3, pp. 68-73 (Mar 1966)

As Received



Sensitized 1 Week at 100° C

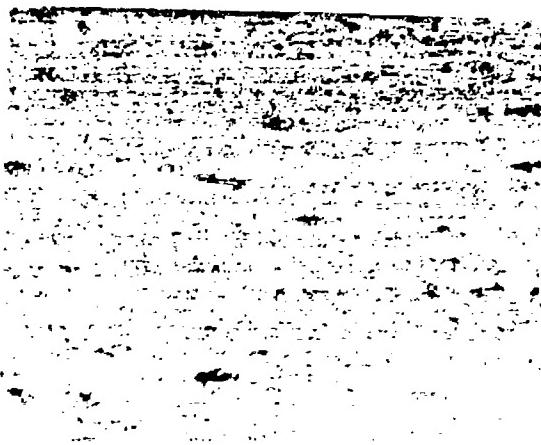


Figure 1
Microstructure of 5456-H321
1/4-Inch Plate (500X)

As Received

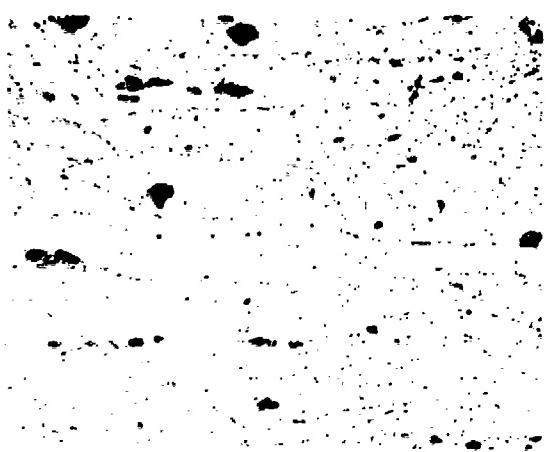


Sensitized 1 Week at 100° C



Figure 2
Microstructure of 5086-H116
1/4-Inch Plate (500X)

As Received



Sensitized 1 Week at 100° C

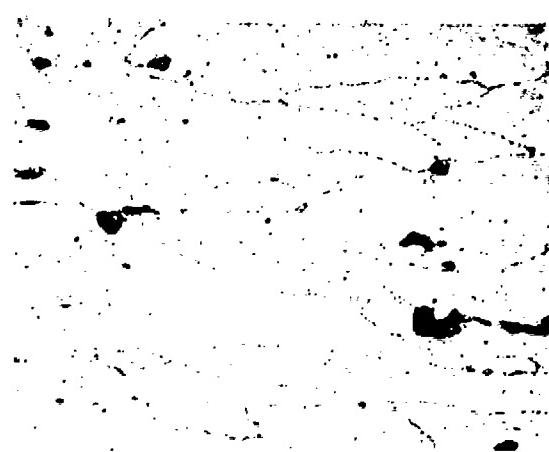


Figure 3
Microstructure of 5086-H116
3/4-Inch Plate (500X)

As Received

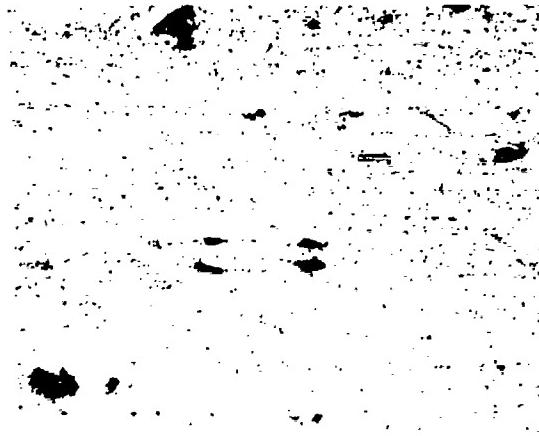


Sensitized 1 Week at 100° C



Figure 4
Microstructure of 5086-H117
1/4-Inch Plate (500X)

As Received

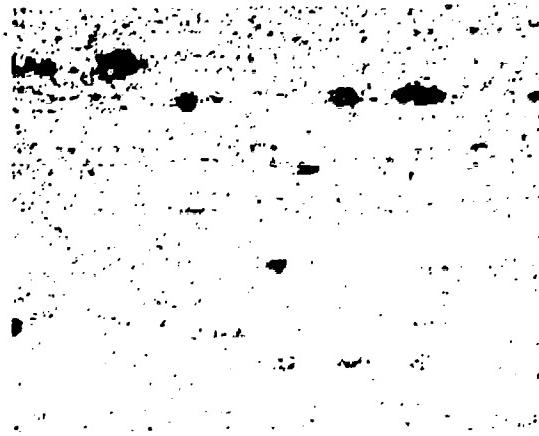


Sensitized 1 Week at 100° C



Figure 5
Microstructure of 5083-H116
1/4-Inch Plate (500X)

As Received



Sensitized 1 Week at 100° C



Figure 6
Microstructure of 5083-H116
1/2-Inch Plate (500X)



As Received

Figure 7
Microstructure of 5456-H116
1/4-Inch Plate (500X)
(Sensitized Condition Not Tested)



As Received

Sensitized 1 Week at 100° C



Figure 8
Microstructure of 5456-H116
1/2-Inch Plate (500X)

As Received

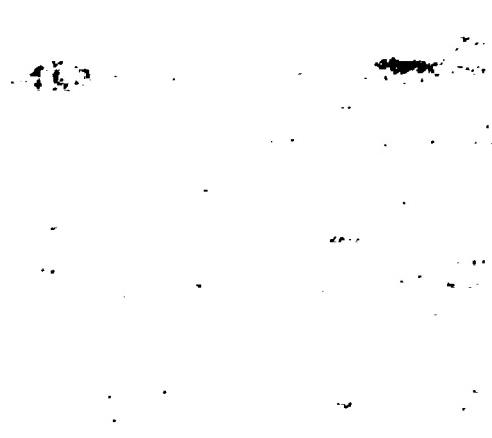


Sensitized 1 Week at 100° C



Figure 9
Microstructure of 5456-H117
1/4-Inch Plate (500X)

As Received



Sensitized 1 Week at 100° C



Figure 10
Microstructure of 5456-H117
1/2-Inch Plate (500X)

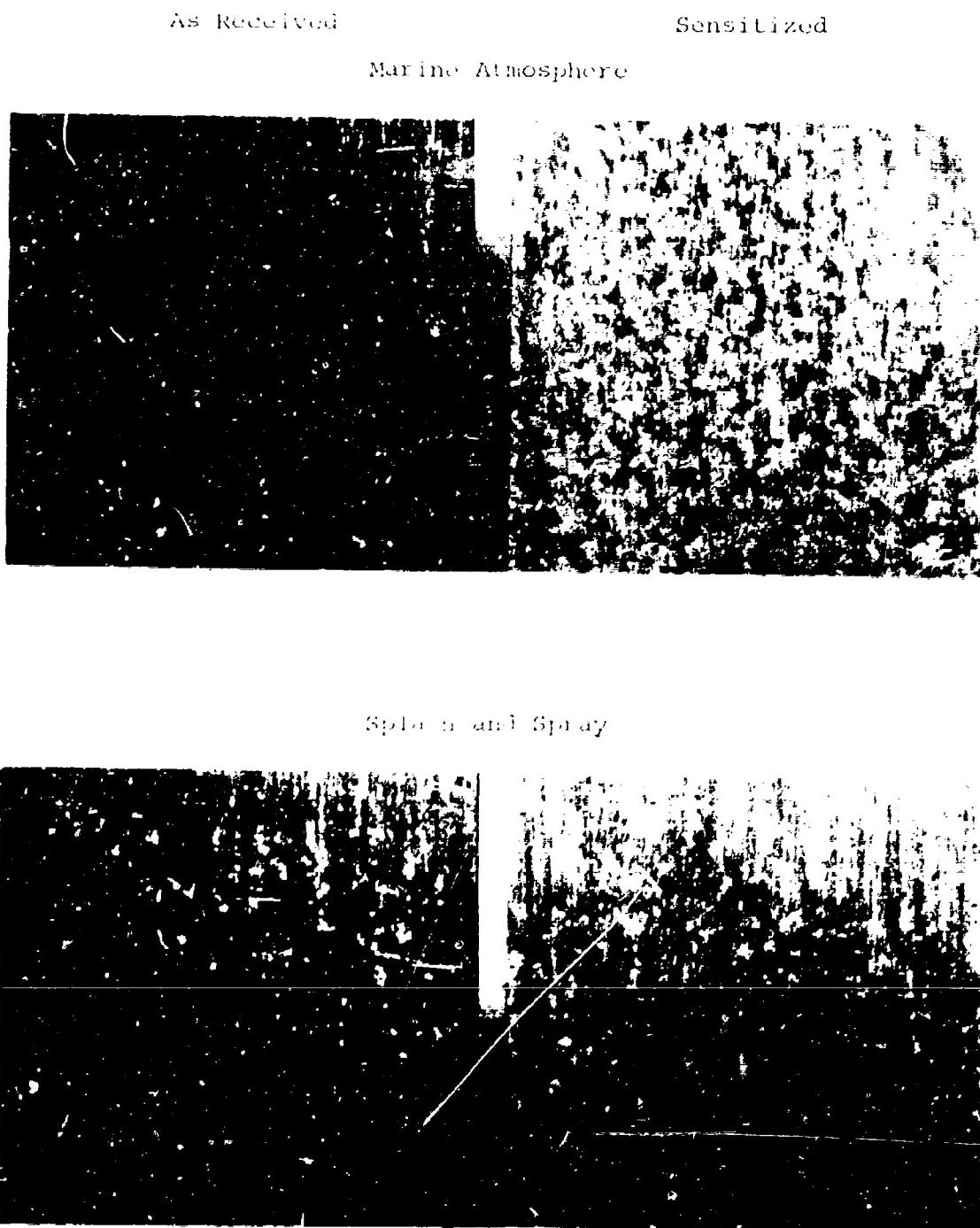


Figure 11
Comparison of Surface Attack on As-Received
and Sensitized 3456-H117 1/4-Inch Plate Exposed
to Splash and Spray and Marine Atmosphere

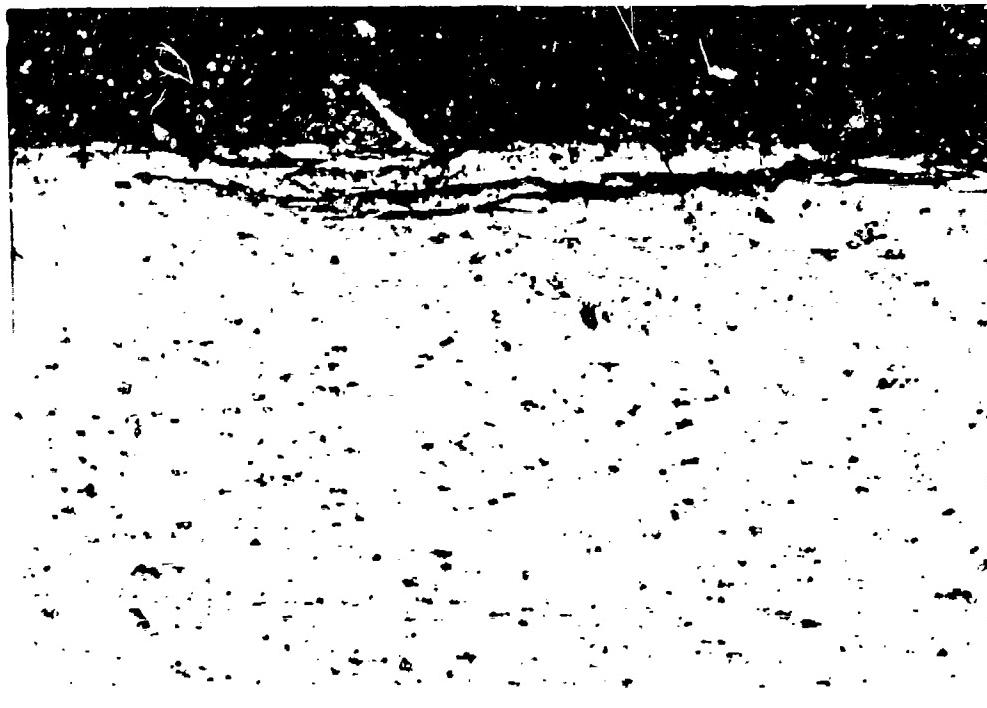


Figure 12
Delamination Under Blistering on
Sensitized 5456-H117 1/4-Inch Plate
After Splash and Spray Exposure
(250X)

As Received

Sensitized

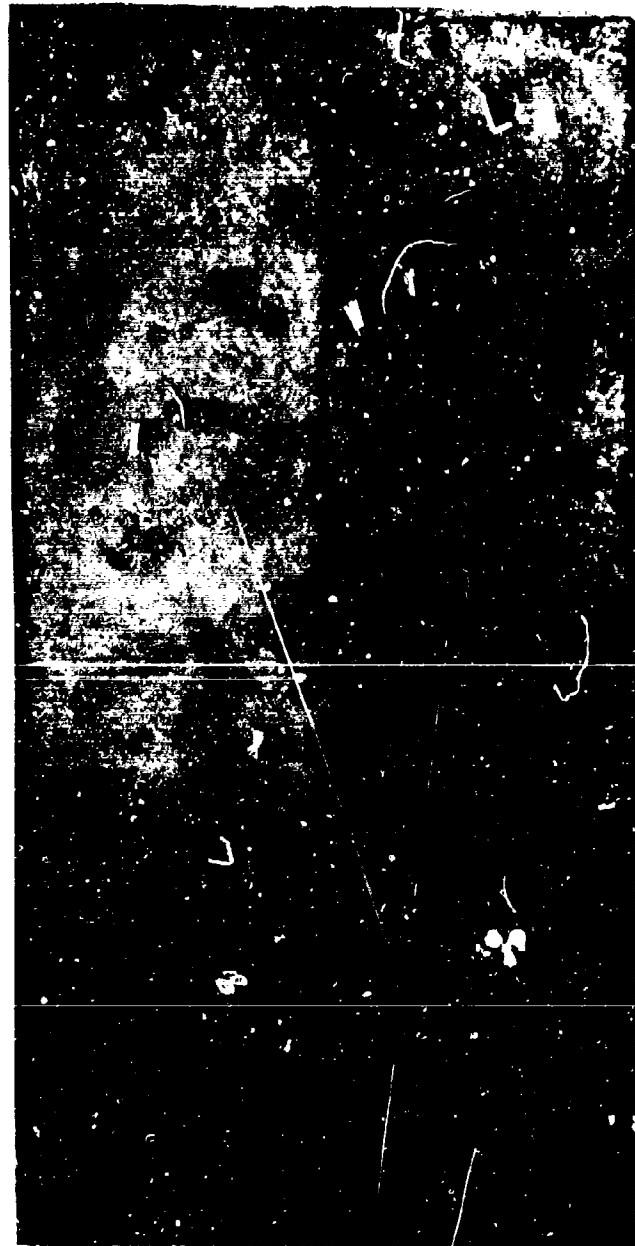


Figure 13
Wide, Shallow Pitting in
Sensitized 5083-H116
1/4-Inch Plate After Fully
Immersed Exposure

Side Edge



A B C D

End Edge



A B C D

Best Available Copy

A = 1/4-Inch Plate, As Received
B = 1/4-Inch Plate, Sensitized
C = 1/2-Inch Plate, As Received
D = 1/2-Inch Plate, Sensitized

Figure 14
Edge Corrosion on 5083-H116 Panels
Exposed to Flowing Sea Water

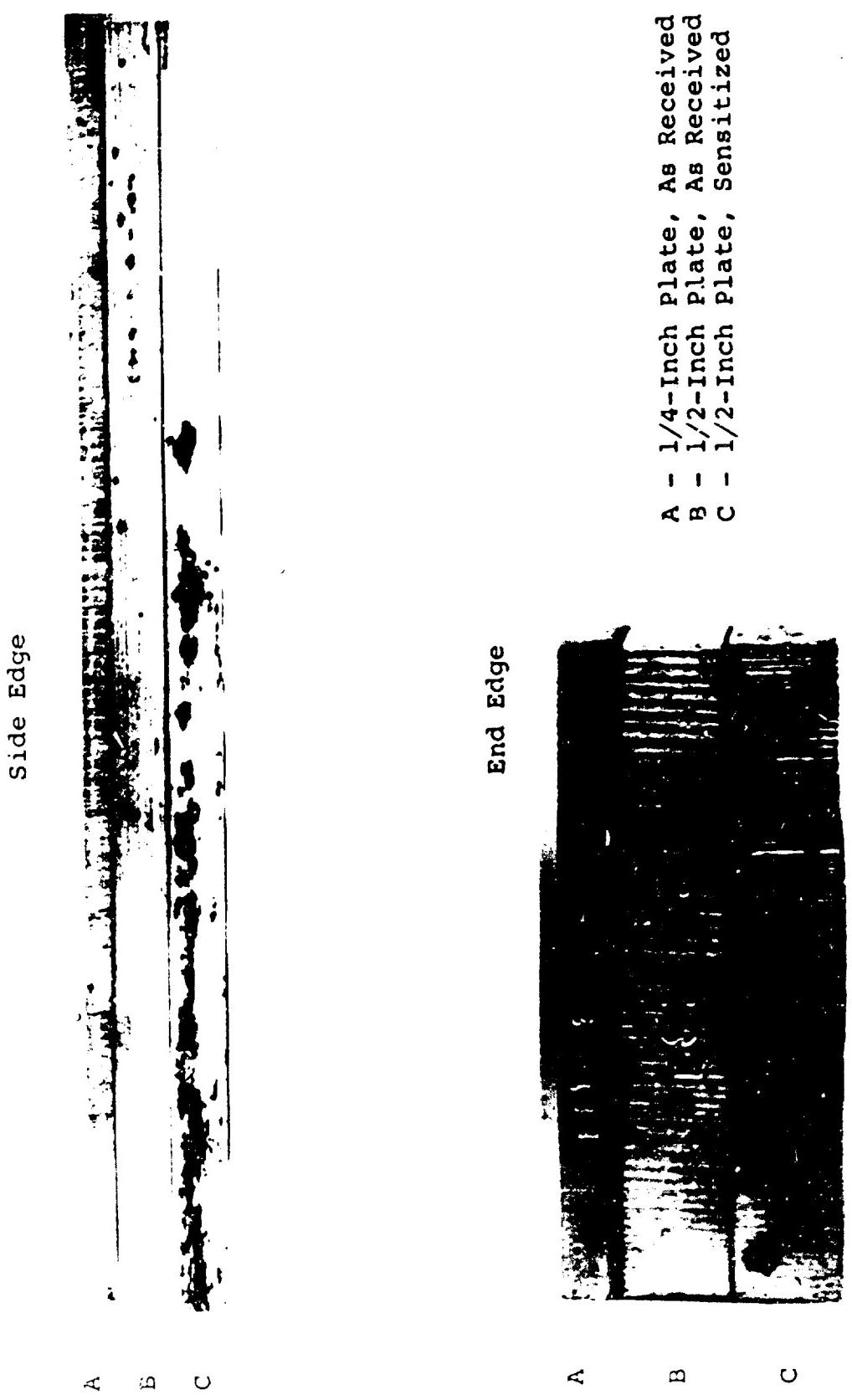


Figure 15
Edge Corrosion on 5466-H116 Panels
Exposed to Flowing Sea Water

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